

Exposure to Halogenated Hydrocarbons in the Indoor Environment

by Kenneth Bridbord,* Paul E. Brubaker,* Bruce Gay, Jr.,* and Jean G. French*

The indoor environment has frequently been ignored as a significant source of exposure to air pollutants. To date there are a number of documented examples of levels of indoor air pollutants greatly exceeding those levels which commonly occur in the outdoor environment. Among these instances are airborne buildup of polynuclear aromatics and cadmium from cigarette smoke, lead from burning candles, and vinyl chloride from use of aerosols containing this substance as a propellant. These examples suggest that there may be additional sources of indoor air pollutants, particularly halogenated hydrocarbons from aerosol products, which have heretofore not been generally recognized as important. The present paper endeavors to review those instances where halogenated hydrocarbons in the indoor air environment may build up to concentrations of potential public health concern. These considerations may be especially relevant in future years as increasing efforts are being made to insulate buildings more efficiently as a means to conserve energy. The available data strongly suggest that halogenated hydrocarbons are an important class of air pollutants in the indoor environment and that their presence in the outdoor environment should also be carefully examined. In this regard, halogenated hydrocarbons in the outdoor environment may also contaminate indoor air spaces.

Introduction

The indoor environment has often been ignored as a significant source of exposure to air pollution, despite the fact that levels of pollutants in the indoor air can frequently exceed those concentrations which commonly occur in the outdoor environment. The present paper endeavors to review those instances where indoor air pollutants and particularly halogenated hydrocarbons, may reach concentrations of potential public health significance. In the past there has been considerable attention given to the potential health hazards of chlorinated aromatic compounds such as PCB's and pesticides. To date, however, there has been relatively little attention given to the halogenated aliphatic compounds which are the primary focus of the present paper.

Behavior of Pollutants in the Indoor Environment

If it is assumed that a given pollutant is chemically stable and evenly distributed in the indoor air, then its decrease in concentration as a function of time due to air dilution is described by eq. (1):

$$C = C_0 e^{-(kQt/V)} \quad (1)$$

where C is concentration at time t , C_0 is initial concentration at time $t = 0$, Q is air turnover rate (ft^3/min), V is room volume (ft^3), t is time (min), and k is a constant to adjust for imperfect mixing.

This simplified equation assumes that the pollutant in question is evenly distributed at time zero and that after time zero the pollutant source is turned off and the air supply into the room is not contaminated by the pollutant in question. If a continuous source after time zero for a given pollutant is also present and/or if the ambient air is contaminated, then the

* National Environmental Research Center, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

problem becomes more complex. In the discussion to follow only the simplified equation will be considered.

In practice, under best mixing conditions, the highest achievable value for k , the mixing constant in eq. (1) is $\frac{1}{2}$ (1). Under these circumstances eq. (1) becomes:

$$C = C_0 e^{-(Q/2V)t} \quad (2)$$

It is apparent from this equation that an important parameter affecting concentration is the turnover rate of air in the room per minute Q/V . If there is no exchange of fresh air, then the equation reduces to a condition in which the concentration at any time is equal to the concentration at time zero assuming complete mixing. The more frequent the exchange for fresh air, the more rapid the concentration of the pollutant decreases.

Let us examine the decrease in concentration with time predicted by eq. (2) under various rates of fresh air exchange. The strong dependence of indoor concentration upon air exchange rate is illustrated in Table 1 and in Figure 1. For example, with but one air exchange per hour, at 30 min the concentration is nearly 80% of its initial value whereas at six air exchanges per hour the concentration has dropped to about 20% of the initial value. After 2 hr, at one air exchange per hour the concentration is still more than one-third the initial concentration (C_0), but at six air exchanges per hour the concentration has fallen below 1% of its initial value.

Given a functional dependence of concentration with time as shown in eq. (2), let us

examine some real world measurements of indoor pollution levels to see if they generally obey this type of relationship. Shown in Table 2 are measurements of propellant concentrations following a 60-sec release of a hairspray in a 29,300-liter room (2). The propellants measured are vinyl chloride and Freon 12. The rate of decay of vinyl chloride parallels that of Freon 12, suggesting that the vinyl chloride was chemically inert over the time frame examined and under the existing experimental conditions. The effect of air exchange upon concentration in this experiment is similar to that predicted by eq. (2) assuming an air exchange rate of six times each hour, and considering that the initial high measurements in the breathing zone at time zero do not reflect complete mixing of the propellants in the room.

Shown in Table 3 are the results of a 30-sec aerosol insect spray released in a home laundry room of 21,400 liter volume (2). The spray was released along the baseboards of the room containing a washer and dryer, sink, clothes, and other miscellaneous items. The room had two doors, one leading to a hallway in the house proper and the other leading to the outside. During the experiment, the door to the hall was closed, and samples were taken by entering the door leading to the outside of the house. Sample 1, collected 1 min after the aerosol was released, showed a concentration of 380 ppm vinyl chloride. Sample 4, taken 150 min after aerosol release, had a concentration of 10.3 ppm vinyl chloride. A sample taken in the hallway adjacent to the laundry room at 151 min contained 0.8 ppm vinyl

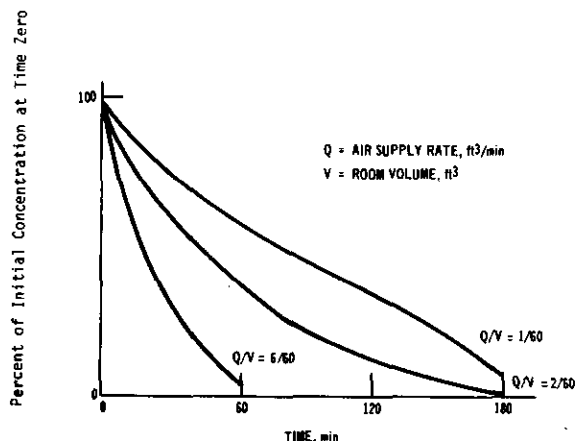


FIGURE 1. Indoor concentration as a function of air exchange rate Q/V and time.

Table 1. Dependence of indoor concentration C upon air exchange rates in a room.

Time, min	C at various air exchange rates		
	Once per hour ($Q/V = 1/60$)	Twice per hour ($Q/V = 2/60$)	Six times per hour ($Q/V = 6/60$)
0	$1.0C_0$	$1.0C_0$	$1.0C_0$
15	$0.88C_0$	$0.78C_0$	$0.47C_0$
30	$0.78C_0$	$0.61C_0$	$0.22C_0$
45	$0.69C_0$	$0.47C_0$	$0.11C_0$
60	$0.61C_0$	$0.37C_0$	$0.05C_0$
90	$0.47C_0$	$0.22C_0$	$0.01C_0$
120	$0.37C_0$	$0.14C_0$	$<0.01C_0$
150	$0.29C_0$	$0.08C_0$	—
180	$0.22C_0$	$0.05C_0$	—

Table 2. Concentration of propellant after 60-sec release of hairspray and deodorants in 29,300 liter room.^a

Sample	Time, min	Propellant concentration, ppm	
		Vinyl chloride	Freon 12
1	Breathing zone during spray	122.7	62.1
2	10	25.8	11.0
3	30	5.6	2.5
4	60	0.1	0.1

^a Data of Gay et al. (2).

Table 3. Concentration of propellant after 30-sec release of insect spray in 21,400 liter room.^a

Sample	Time, min	Propellant concentration, ppm	
		Vinyl chloride	Freon 12
1	1	380.1	466.4
2	31	52.1	54.4
3	61	24.6	26.4
4	151	10.3	11.5
5	151 ^b	0.8	0.9

^a Data of Gay et al. (2).

^b Collected in adjacent hall.

chloride, indicating spread of vinyl chloride to other areas of the house despite the closed door. If it is assumed that the initial measurement was not made at a time when there was equal mixing throughout the room, the rate of decay of concentration with time was similar to that which would be expected at an air turnover of twice per hour according to eq. (2).

In contrast to the experiment with the hairspray, in which Freon 12 concentrations were about one-half those of the vinyl chloride, Freon 12 levels in the insect spray experiment were 10–20% greater than the vinyl chloride concentrations. Given the frequent sequential use of aerosol products containing Freons such as hairsprays and deodorants, peak exposures to Freon mixtures well in excess of 100 ppm might result following combined use of such aerosol products in the indoor environment.

Shown in Table 4 is a breakdown of propellant use in aerosol products as a function of product category (3). It is apparent from this table that a number of halogenated hydro-

Table 4. Use of propellants in aerosol products by product category.

Product classification	Propellants used	Frequency used
Inhalants containing bronchodilator drugs (11 products)	Freon 11 (trichlorofluoromethane)	5/11
	Freon 12 (dichlorofluoromethane)	11/11
	Freon 114 (dichlorotetrafluoroethane)	9/11
Mouth products (6 products)	Freon 12	5/6
	Freon 114	5/6
	Freon 1426 (monochlorodifluoroethane)	1/6
Vaporizers (2 products)	Freon 11	2/2
	Freon 12	2/2
	Trichloroethane	1/2
Hair products (62 products)	Freon 11	53/62
	Freon 12	54/62
	Freon 114	4/62
	Freon 152a (difluoroethane)	5/62
	Methylene chloride	8/62
	Vinyl chloride	1/62
Women's personal hygiene products (22 products)	Propane	3/62
	Isobutane	32/62
	Freon 11	5/22
	Freon 12	20/22
	Freon 114	6/22
	Isobutane	2/22
Deodorants and antiperspirants (38 products)	Freon 11	13/38
	Freon 12	37/38
	Freon 114	8/38
	Freon 142b	1/38
	Propane	1/38
	Isobutane	1/38
Foot products (9 products)	Freon 11	8/9
	Freon 12	9/9
	Freon 114	1/9
Miscellaneous products for personal use (18 products)	Freon 11	7/18
	Freon 12	15/18
	Freon 114	3/18
	Isobutane	2/18
	Propane	2/18

carbons are employed as aerosol propellants. Depending upon the frequency and patterns of use of aerosol products among the population, a substantial number of individuals may be exposed repeatedly to these compounds. By far the most commonly used propellants as illustrated in Table 5 are Freon 11 and Freon 12, although vinyl chloride has also been identified as one of the propellants which has been used in experiments conducted by the Environmental Protection Agency and elsewhere (3).

Recently published studies of instantaneous Freon 11 and Freon 12 concentrations in the indoor environment taken at random confirm the presence of measurable quantities of these

pollutants in the indoor air (4). Levels of Freon 12 in homes, for example, exceeded 500 ppb and were generally much greater than simultaneous outdoor concentrations which usually measured 1 ppb or less. In one study, a measurement of Freon 12 in a beauty shop indicated a concentration of 370 ppb (4). A study conducted by the Environmental Protection Agency of Freon 12 levels in a beauty shop found a concentration of 3000 ppb or 3 ppm. No vinyl chloride was identified in this experiment.

Apart from aerosol propellants, exposure to halogenated hydrocarbons in the indoor environment may occur from the active ingredients contained in aerosol products. For example, aerosol spot removers used for cleaning clothing, carpets, upholstery and wallpaper may frequently contain perchloroethylene as the active ingredient. The concentration of perchloroethylene in such products could be similar to the quantity of propellant in these products. Under these circumstances, peak concentrations of perchloroethylene in excess of 100 ppm might occur during and immediately following spraying, as judged from the data in Tables 2 and 3. It is noteworthy that the threshold limit value for perchloroethylene is 100 ppm with excursions recommended not to exceed 150 ppm (5). Accordingly, aerosol products containing perchloroethylene may, under certain circumstances, result in exposures among the general population which exceed established exposure limits for workers.

Another source of indoor exposure to halo-

genated hydrocarbons may be from solvents. Such products contain volatile components which could build up to high concentrations in the indoor air. Consider a substance such as trichloroethylene (TCE), a structural analog to vinyl chloride, which is used for a variety of purposes, in dry cleaning, as a degreasing agent, and as an anesthetic. At 12°C (54°F) TCE has a vapor pressure of 40 mm Hg, and at 20°C (68°F) TCE has a vapor pressure of 60 mm Hg. In contrast, water at 12°C has a vapor pressure of 11 mm Hg and at 20°C, a vapor pressure of 18 mm Hg. Consequently the tendency for trichloroethylene to vaporize is greater than that of water, which does not attain a vapor pressure of 60 mm Hg until 42°C (108°F). Should the atmosphere above trichloroethylene reach only 0.1% of saturation, then at 20°C the concentration of trichloroethylene would be nearly 80 ppm. The threshold limit value for TCE is currently 100 ppm (5). Naturally, with good ventilation TCE would never reach 80 ppm, but under certain situations, air exchange may be low and TCE used in a closed space could build up to appreciable airborne concentrations.

Shown in Table 6 are the indoor levels for some commonly used solvents predicted by assuming that these attain a concentration only 0.1% of their saturation level in the air. In this regard it is noteworthy that carbon tetrachloride, trichloroethylene, and tetrachloroethylene (perchloroethylene) have been detected in both the ambient and the indoor air (4,6).

For example, one study in Los Angeles County in 1966 estimated that emissions of hydrocarbons into the atmosphere from organic solvent usage comprised better than 20% of all

Table 5. Overall use of propellants in 168 aerosol products.

Propellant	Frequency of use	%
Previously published data (3)		
Freon 11	93/168	55.4
Freon 12	153/168	91.1
Freon 114	36/168	21.4
Freon 1426	2/168	1.2
Freon 152a	5/168	3.0
Isobutane	37/168	22.0
Methylene chloride	8/168	4.8
Propane	6/168	3.6
Trichloroethane	1/168	0.6
Vinyl chloride	1/168	0.6
Environmental Protection Agency studies		
Freon 11	25/61	41.0
Freon 12	50/61	82.0
Vinyl chloride	4/61	6.5

Table 6. Predicted indoor concentrations of halogenated hydrocarbon solvents assuming that they reach 0.1% of saturation levels.

Solvent	Temperature, °C	Predicted indoor air concentration, ppm
Trichloroethylene	20	80
Tetrachloroethylene	26	26
1,1,2-Trichloroethane	21	26
1,1,1-Trichloroethane	20	130
Carbon tetrachloride	23	130
Methylene chloride	24	520

hydrocarbon emissions (7). Of the estimated 590 tons emitted per day from organic solvents, 88 tons per day were attributed to halogenated hydrocarbons, including trichloroethylene and tetrachloroethylene. Given the similarity of chemical structure between trichloroethylene and vinyl chloride, a recently recognized carcinogen, one would desire to study the health implications of this substance in much greater depth (8).

In a study of the airborne environment near a solvent recovery plant in Maryland, levels of carbon tetrachloride were measured in the ambient and the indoor air. The levels of carbon tetrachloride indoors were sometimes three to four times those which were measured outdoors. At times concentrations of CCl_4 of 10–45 ppm were measured inside a house near the plant when levels outside were 1 ppm. The highest indoor concentration of carbon tetrachloride recorded was 90 ppm.

A potentially important source of indoor exposure to halogenated hydrocarbons may be from use of such compounds as anesthetic agents. It has already been noted that trichloroethylene continues to be used as an anesthetic, particularly in oral surgery. Vinyl chloride, a structural analog to trichloroethylene and a recently identified carcinogen and liver toxin, has similar neurologic action and once was considered for use as an anesthetic. Ethylene, though not containing chlorine, has also been used as an anesthetic. Under these circumstances one wonders whether potential for carcinogenic activity and/or liver toxicity exists for unsaturated halogenated compounds with anesthetic activity such as trichloroethylene (8). If so, a possible health risk may exist not only for patients but also for personnel who routinely administer these compounds. A number of other halogenated compounds besides trichloroethylene are also used as anesthetics. These compounds include halothane and methoxyflurane. Though not unsaturated, these latter compounds may require reexamination in terms of their potential for toxic activity, particularly to the liver. Methoxyflurane combines an ether structure with that of a halogenated aliphatic compound and its structural similarity to the chloromethyl ethers should not be overlooked. Chloroform, also halogenated, is yet another anesthetic which is toxic to the liver. It is noteworthy that divinyl ether, while not a

halogenated compound, in some respects is analogous in structure to trichloroethylene and vinyl chloride and also represents an anesthetic with established liver toxicity.

It is evident from this brief discussion that a number of halogenated hydrocarbons have been documented and/or are suspected to be present in the airborne environment both indoors and out. The available data suggest that indoor levels of these substances are frequently greater than are found outdoors, though indoor contamination may frequently originate from outdoor sources.

Health Implications

In assessing the risk to health for the general population from exposure to a given air pollutant, one must consider the inherent toxicity of the material in question, the range of concentrations which may be present in the air, and the probability that members of the population may be exposed to these concentrations. If one were to examine the halogenated hydrocarbons on the basis of the above criteria, many compounds in this class would have to be suspected as potential health risks for the general population.

Observations such as those discussed in this paper suggest that the general population is currently exposed to halogenated hydrocarbons in the indoor environment. The health implications of many of these compounds are not well understood. For example, the preponderance of studies on Freons, commonly used as aerosol propellants, involve consideration of acute, but not chronic effects (3). Though Freons are considered to be chemically inert in the environment, this may not be true in biological systems. Available data suggest that short-term exposures to Freons in man may result in cardiac arrhythmias (3). The possible effect of such exposures upon individuals already prone to arrhythmias such as those with atherosclerotic heart disease must thus be considered and requires additional study. Use of aerosol products containing methylene chloride may also stress the cardiovascular system by increased endogenous formation of carbon monoxide (9). Other halogenated hydrocarbons should also be examined for their potential effects upon CO metabolism. Home cleaning agents in aerosol form have the potential to exceed accepted

occupational exposure limits for perchloroethylene. Clearly the multitude of aerosol products commercially available represent an important source of exposure to halogenated hydrocarbons, as do solvents and anesthetics. Exposure to these substances is greatly accentuated in the indoor environment where there is less opportunity for dispersion. Since the activity patterns of the general population include a substantial portion of time spent indoors, the cleanliness of the indoor air becomes an important consideration.

REFERENCES

1. Corn, M. In: Toxicity of Vinyl Chloride-Polyvinyl Chloride. Ann. N.Y. Acad. Sci. 246: 303 (1975).
2. Gay, B., et al. Measurements of vinyl chloride from aerosol sprays. In: Toxicity of Vinyl Chloride-Polyvinyl Chloride. Ann. N.Y. Acad. Sci. 246: 286 (1975).
3. Aviado, D. M. Toxicity of propellants. In: Proceedings of the 4th Annual Conference on Environmental Toxicology, Aerospace Medical Research Laboratory, Wright Patterson Air Force Base, Ohio, 1973.
4. Hester, N. E., Stephens, E. R., and Taylor, O. C. Fluorocarbons in the Los Angeles Basin. J. Air Poll. Control Assoc. 24: 591 (1974).
5. Anonymous. TLV's threshold limit values for chemical substances in workroom air adopted by the American Conference of Government Industrial Hygienists for 1973. J. Occ. Med. 16: 39 (1974).
6. Capurro, P. U. Effects of exposure to solvents caused by air pollution with special reference to CCl₄ and its distribution in air. Clin. Toxicol. 6: 109 (1973).
7. Brunelle, M. Effectiveness of organic solvents in photochemical smog formation. Solvent Project, Final Report, Air Pollution Control District, County of Los Angeles July 1966.
8. Van Duuren, B. L. On the possible mechanism of carcinogenic action of vinyl chloride. In: Toxicity of Vinyl Chloride-Polyvinyl Chloride. Ann. N.Y. Acad. Sci. 246: 258 (1975).
9. Stewart, R. D., and Fisher, T. N. Carboxyhemoglobin elevation after exposure to dichloromethane. Science. 175: 295 (1972).